



Nanoscience Open House • Naval Research Laboratory



Nanoscience Research in the NRL Chemistry Division

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<http://www.chemistry.nrl.navy.mil/6170>



Nanoscience Activities by Section

Materials Chemistry Branch, Code 6120

- Code 6123: Materials Synthesis and Processing (**Art Snow**)
 - *Gold nanocluster chemical sensors* (*Art Snow*)
 - *Self-assembly/characterization of nanocluster architectures* (*Ed Foos & Ann Mera*)
- Code 6125: Functional Materials (**John Russell**)
 - *Spatially-controlled organic chemistry on semiconductor surfaces*
- Code 6127: Advanced Materials (**Teddy Keller**)
 - *Metal nanoparticle composites*
- Code 6109: Theoretical Chemistry (**Carter White**)
 - *Carbon nanostructures* (*Brett Dunlap & Carter White*)



Nanoscience Activities by Section

Surface Chemistry Branch, Code 6170

- Code 6171: Advanced Electrochemical Materials (**Debra Rolison**)
 - *Nanostructured mesoporous materials* (*Debra Rolison/Jeffrey Long*)
- Code 6174: Gas/Surface Dynamics (**Jim Butler**)
 - *Nanofilaments* (*Pehr Pehrsson*)
 - *Carbon nanotube field emitter arrays* (*David Hsu*)
 - *Nanocrystal synthesis* (*Al Berry*)
- Code 6176: Tribology & Surface Coatings (**Irwin Singer**)
 - *Nanomechanics/nanotribology* (*Kathy Wahl*)
- Code 6177: Surfure Nanoscience & Sensor Technology (**Lloyd Whitman**)
 - *High-index silicon & germanium surfaces* (*Arnaldo Laracuente*)
 - *III-V heterostructures/cross sectional STM* (*Lloyd Whitman*)
 - *Dip pen nanolithography* (*Paul Sheehan*)
 - *InAs nanostructure sensor* (*Dmitri Petrovykh*)
 - *Single molecule biosensors* (*Cole, Malito, Mulvaney, Piani, Rife, Tamanaha, Whitman*)



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Outline



- Imaging & Nanofabrication
 - **H-Induced Morphology: Si(001)-to-(115)** ([Arnaldo Laracuente/Lloyd Whitman](#))
 - **III-V Heterostructures/cross sectional STM** ([Lloyd Whitman](#))
 - **Spatially-controlled organic surface chemistry** ([John Russell](#))
 - **Dip pen nanolithography** ([Paul Sheehan](#))
 - **Nanomanipulator** ([Pehr Pehrsson](#))
- Materials & Materials Properties
 - **Nanomechanics/nanotribology** ([Kathy Wahl](#))
 - **Nanostructured mesoporous materials/aerogels** ([Debra Rolison/Jeffrey Long](#))
 - **Nanocrystal synthesis** ([Al Berry](#))
 - **Metal nanoparticle composite materials** ([Teddy Keller](#))
 - **Nanofilaments** ([Pehr Pehrsson](#))
 - **Carbon nanostructures** ([Cater White](#))
- Sensors & Devices
 - **Carbon nanotube field emitter arrays** ([David Hsu](#))
 - **Gold nanocluster chemical sensors** ([Art Snow](#))
 - **Self-assembly/characterization of nanocluster architectures** ([Ed Foos/Ann Mera/Art Snow](#))
 - **Single molecule biosensors** ([Cole, Colton, Malito, Mulvaney, Piani, Rife, Tamanaha, Whitman](#))
 - **InAs nanostructure sensor** ([Dmtri Petrovykh](#))



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Imaging & Nanofabrication



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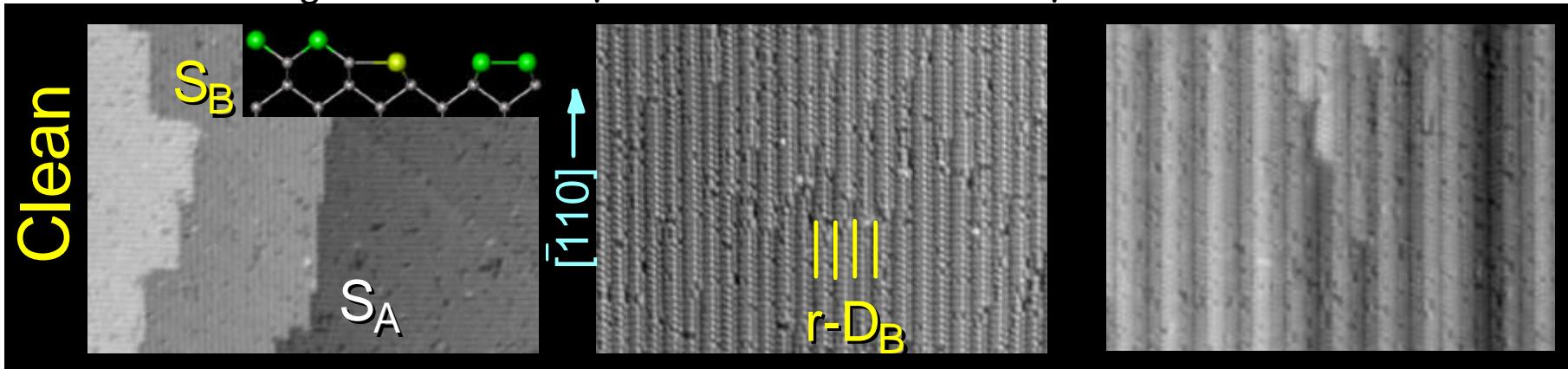


H-Terminated High-Index Si Structures

Filled State Images

500 Å

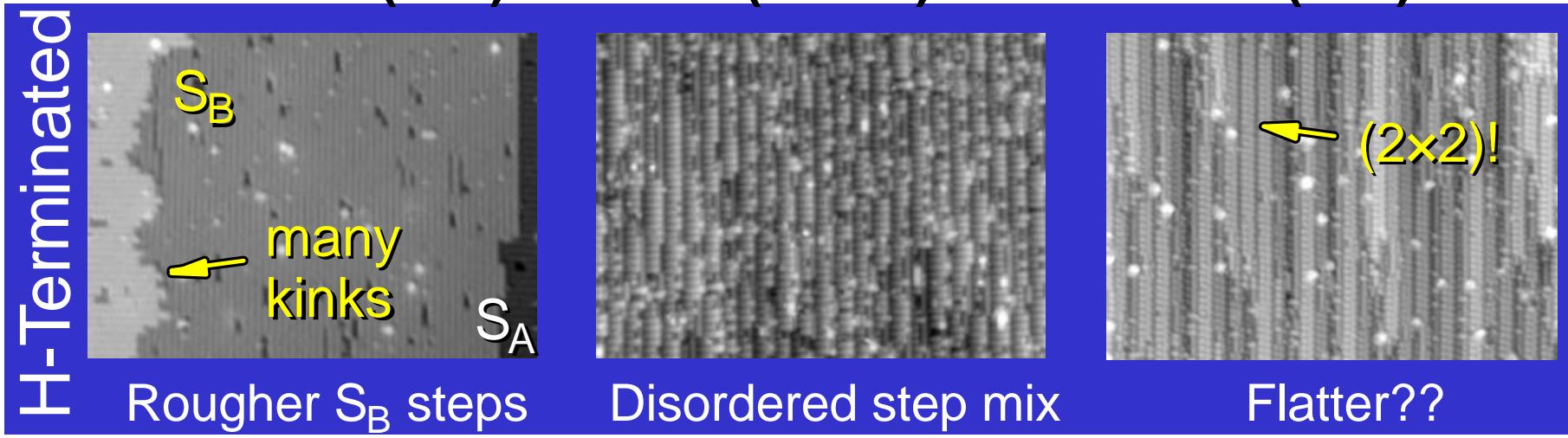
Laracuente & Whitman - 6177



nominal (001)

(1 1 11)

(115)

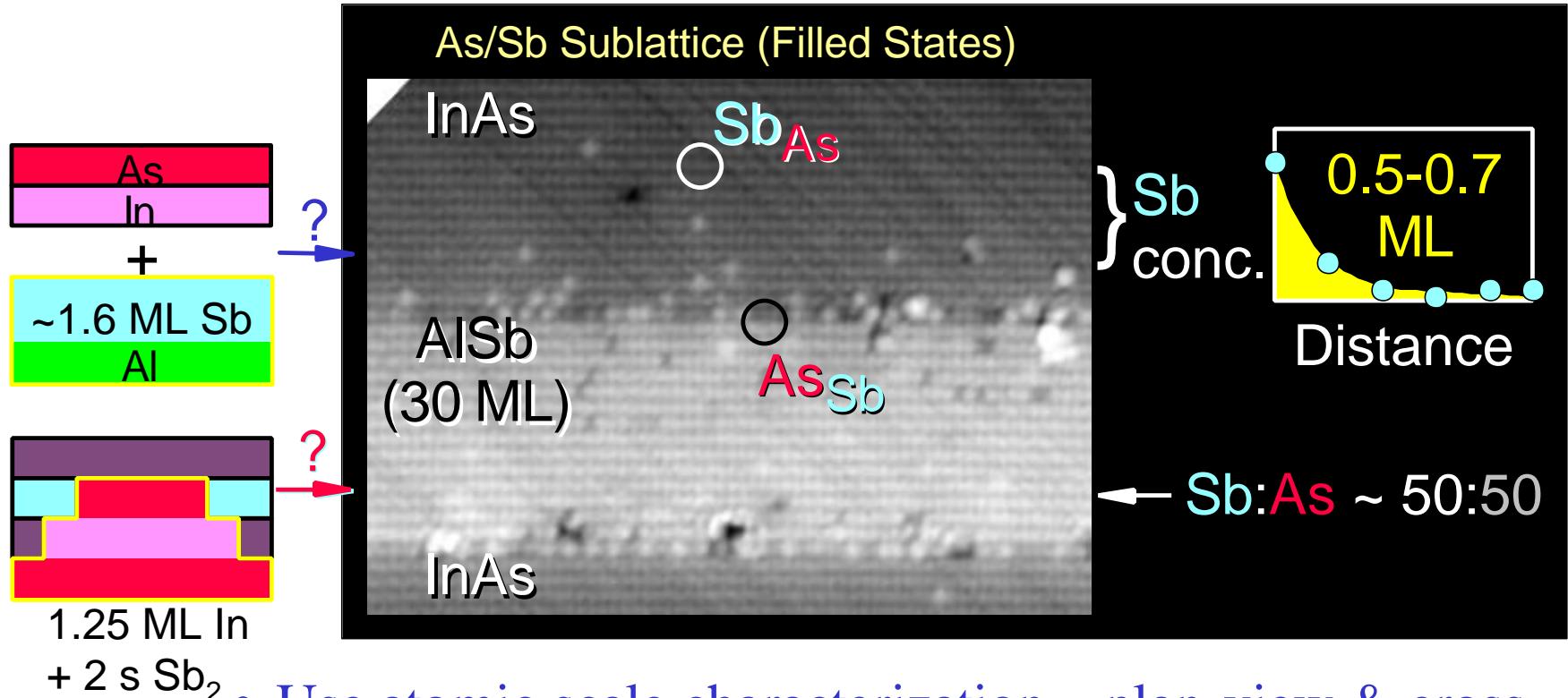


H changes relative energies of step structures

Surf. Sci. 476,
L247 (2001)



AlSb-InAs Interfacial Structure: XSTM

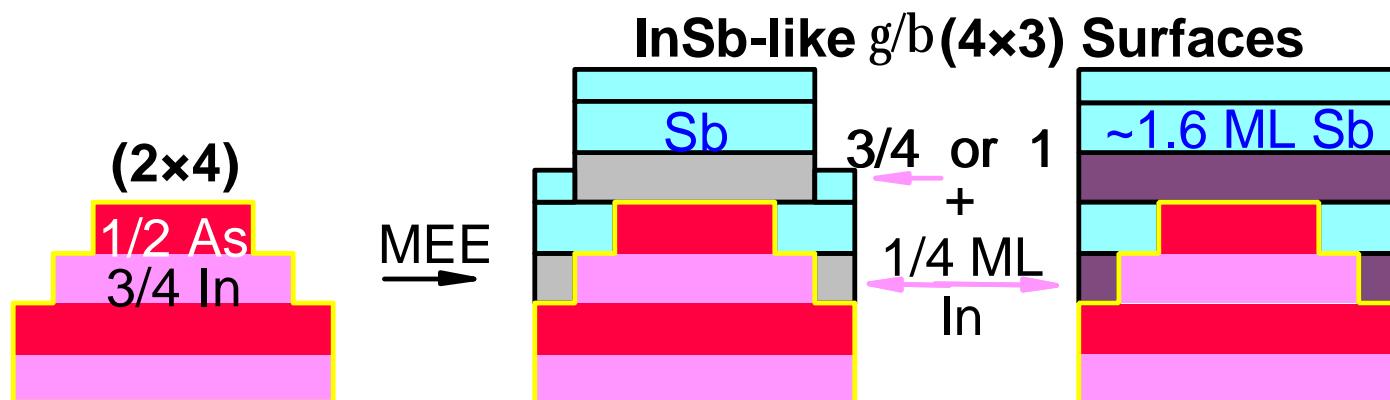
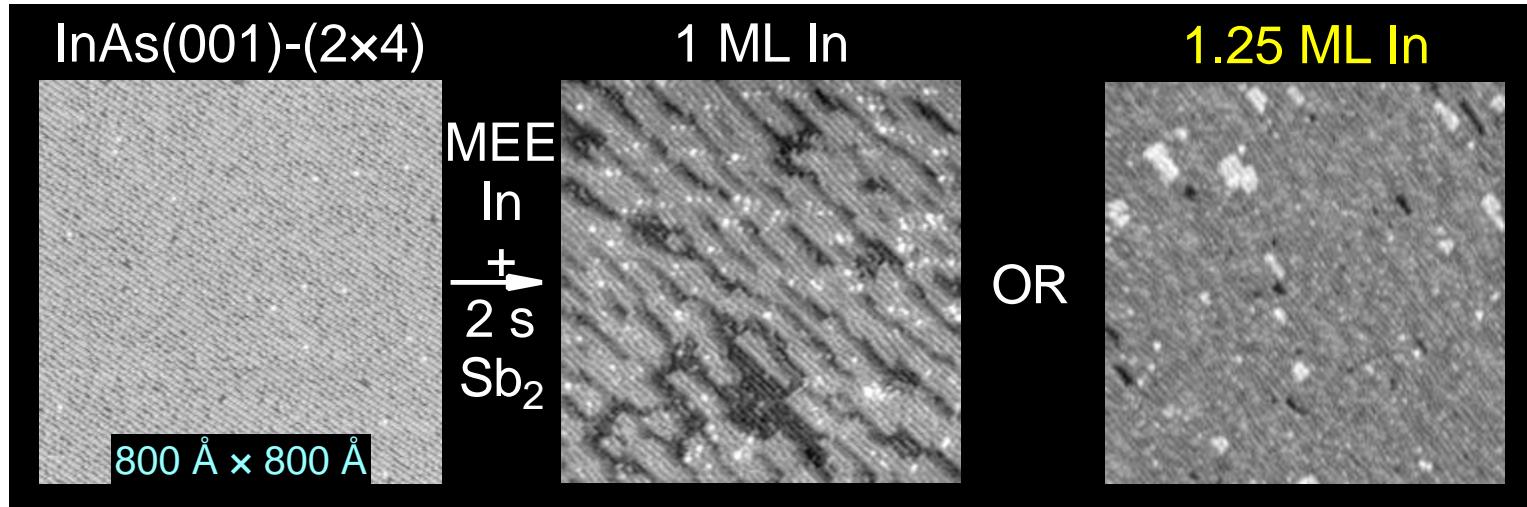


- Use atomic-scale characterization—plan-view & cross sectional STM results—to control interfacial structure
- Roughness due to change in reconstruction stoichiometry

B.Z. Noshko, W. Barvosa-Carter, M.J. Yang, B.R. Bennett & L.J. Whitman, *Surf. Sci.* **465**, 361 (2000);
W. Barvosa-Carter, M.E. Twigg, M.J. Yang & L.J. Whitman, *PRB* **64**, 245311 (2001)



AlSb-InAs Interfacial Roughness

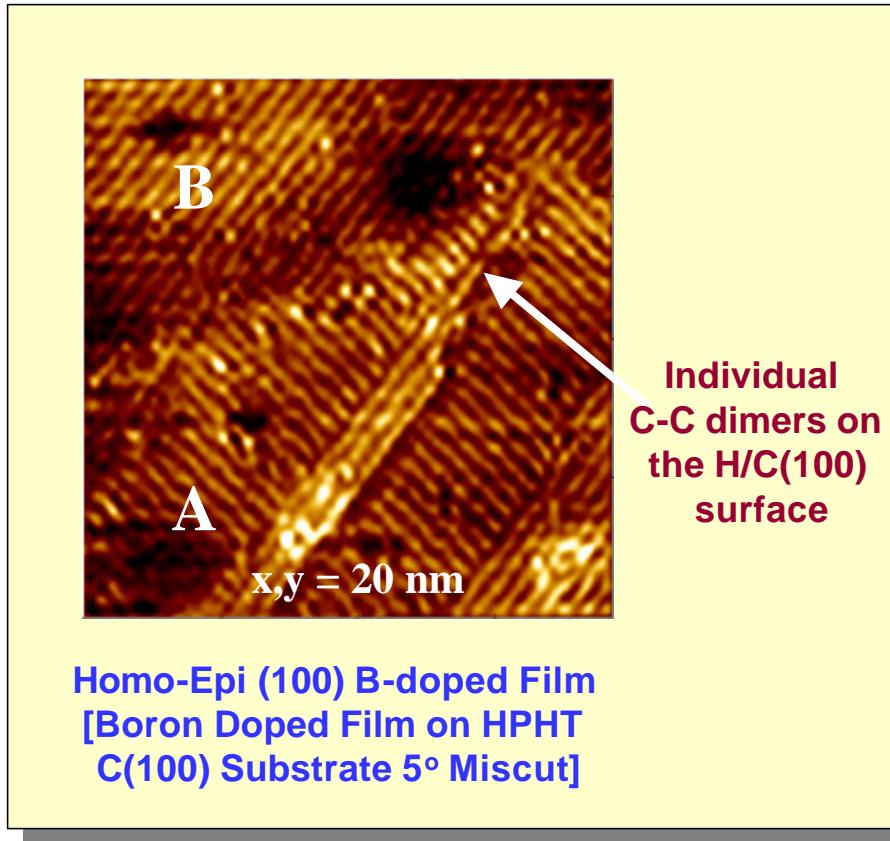


Roughness due to change in reconstruction stoichiometry

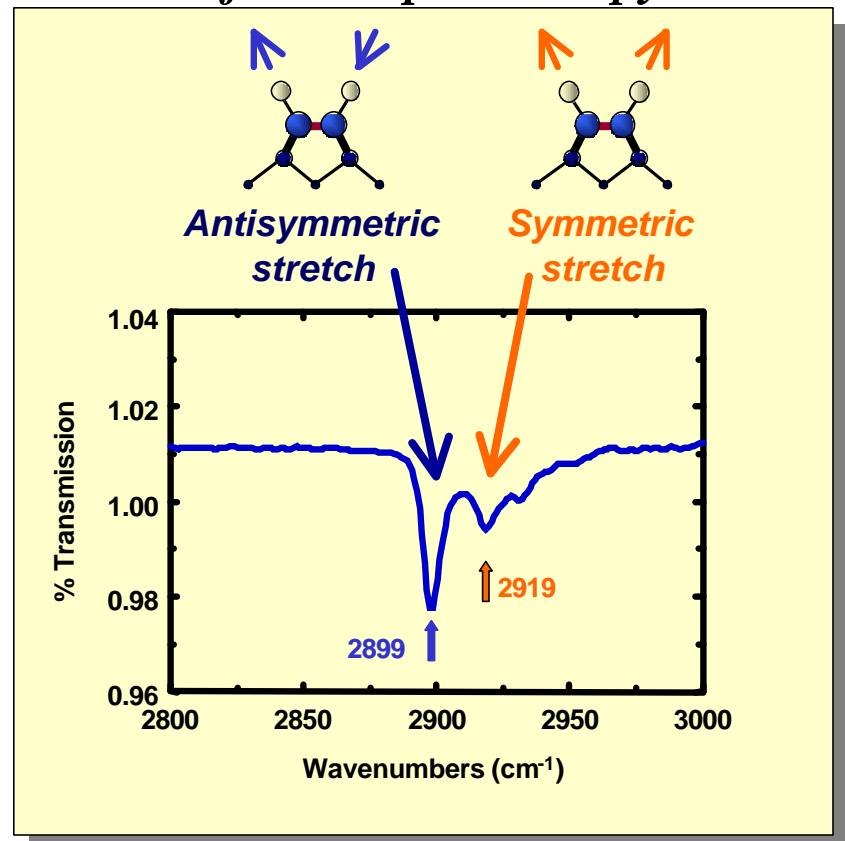


Hydrogen on Diamond (100)

Scanning Tunneling Microscopy



Multiple Internal Reflection Infrared Spectroscopy



Demonstrate hydrogen termination of surface dimers

J.N. Russell, Jr. (NRL Code 6125); J.E. Butler & P.E. Pehrsson (NRL Code 6174)

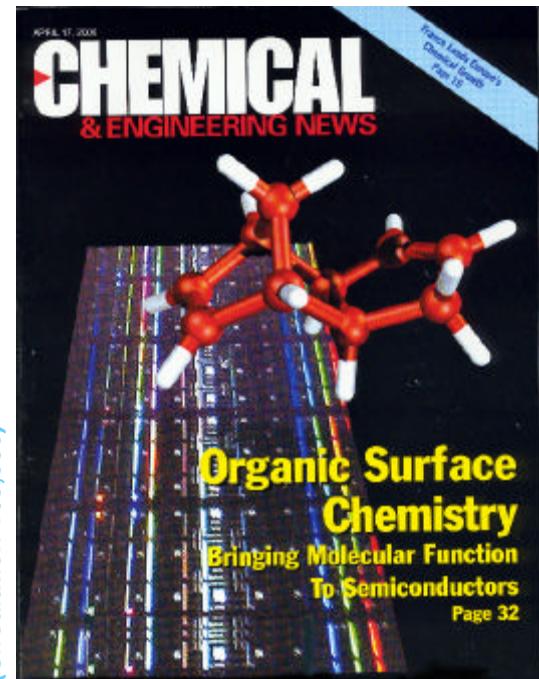


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Spatially-Controlled Organic Chemistry

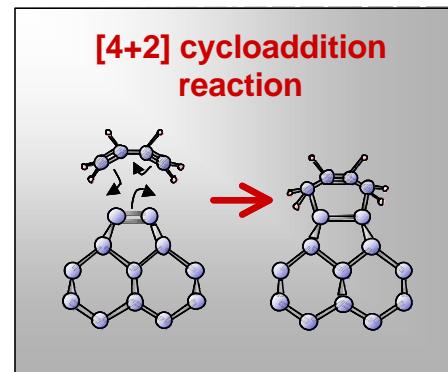
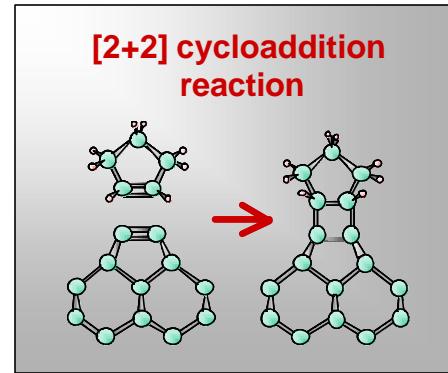
Cycloaddition reactions between certain organic compounds and “double” bonded surface dimers result in two bonds to the surface, registering and constraining the orientation of the molecules on the surface



(Circulation 163,000)

Main highlight of Spring 2000 ACS meeting!

J.N. Russell, Jr., NRL Code 6125



On Diamond (100):

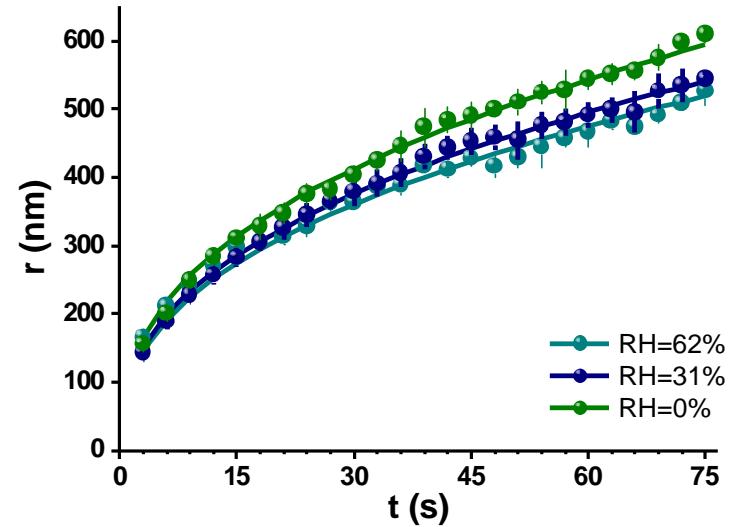
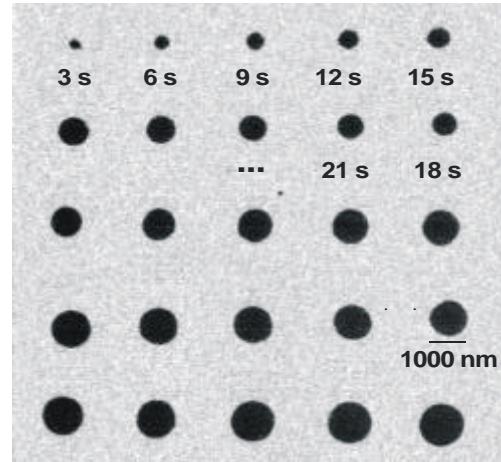
- J.S. Hovis, *et al.*, *J. Am. Chem. Soc.* **122**, 732 (2000)
- G.T. Wang, *et al.*, *J. Am. Chem. Soc.* **122**, 744 (2000)



Dip Pen Nanolithography

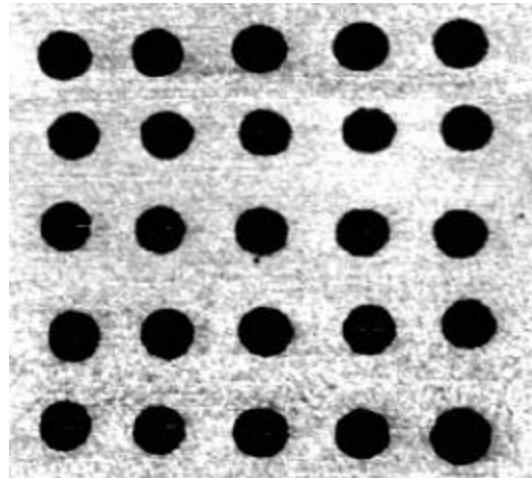
Friction
Image of
ODT islands

P.E. Sheehan &
L.J. Whitman,
Phys. Rev. Lett.,
submitted

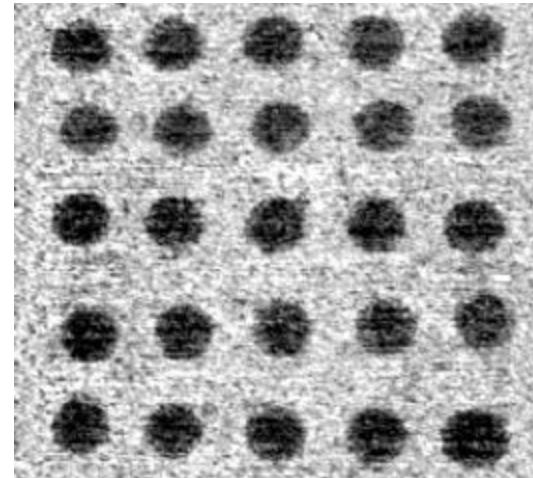


Transfer is not through the meniscus

in humid
air (RH:
38%)



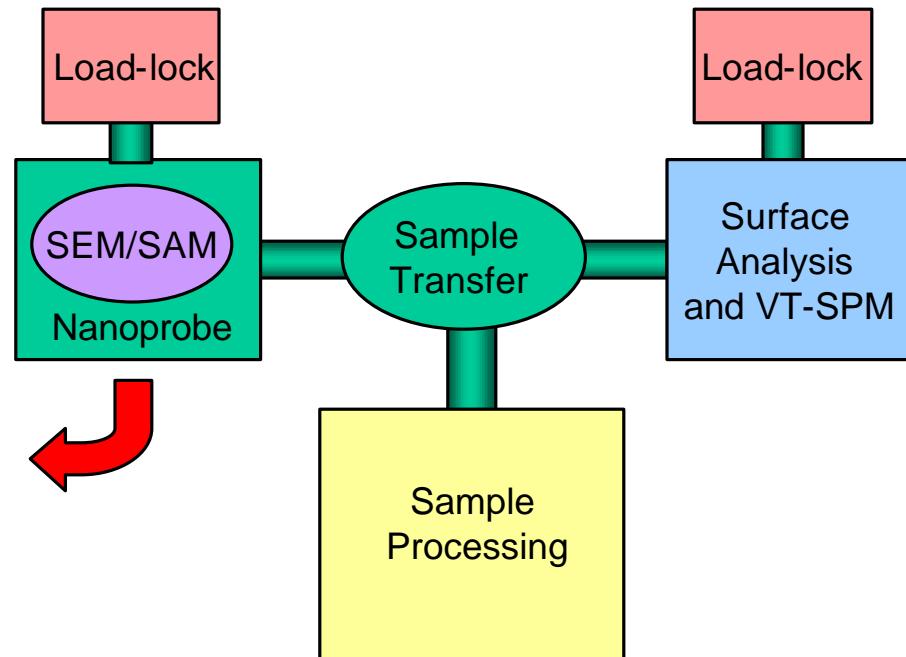
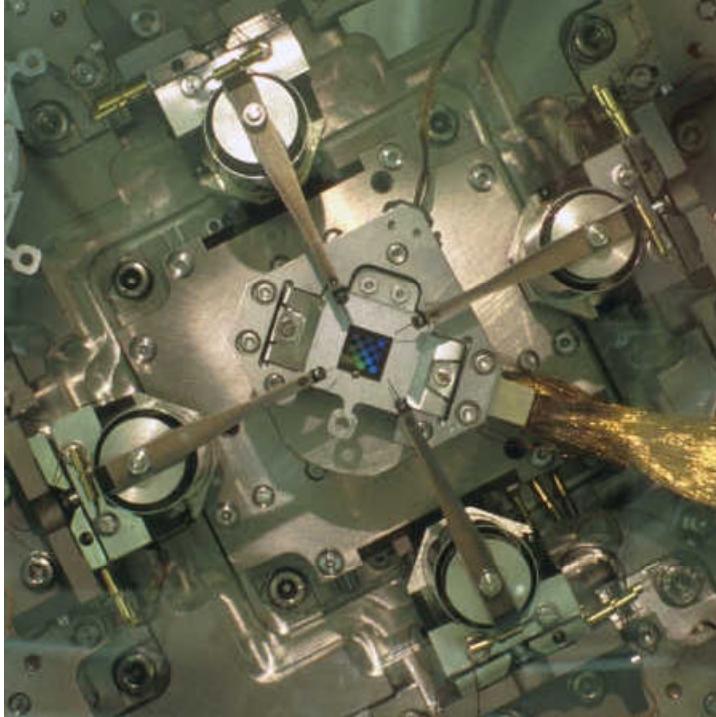
↑
13.5 μm
↓



in dry
air (0%)
for 24h



Nanocharacterization/Manipulator Facility



Top view of stage with 4 individually-controlled STM probes and coaxial SEM. System also has a variable temperature STM/AFM

- Structural information and imaging
- 4-point electrical conductivity
- Nanomanipulation
- *In-situ* sample prep and surface analysis

Pehrsson – 6174
Wahl – 6176
Whitman – 6177



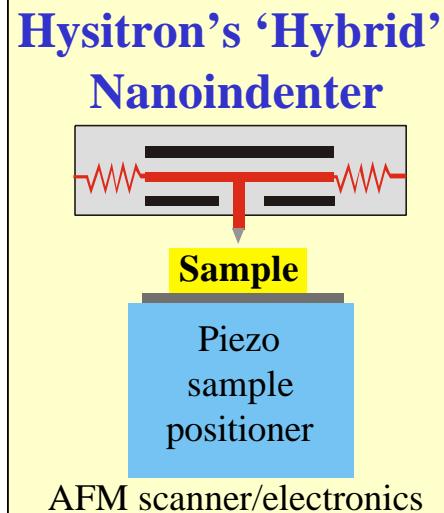
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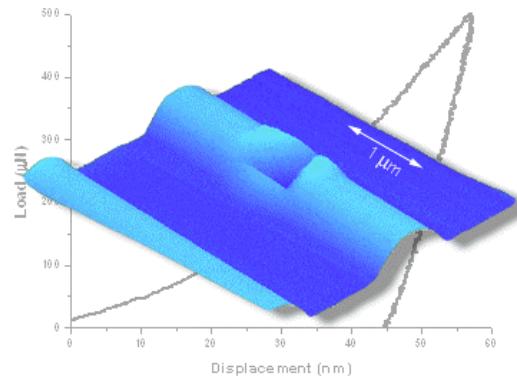
Materials & Materials Properties



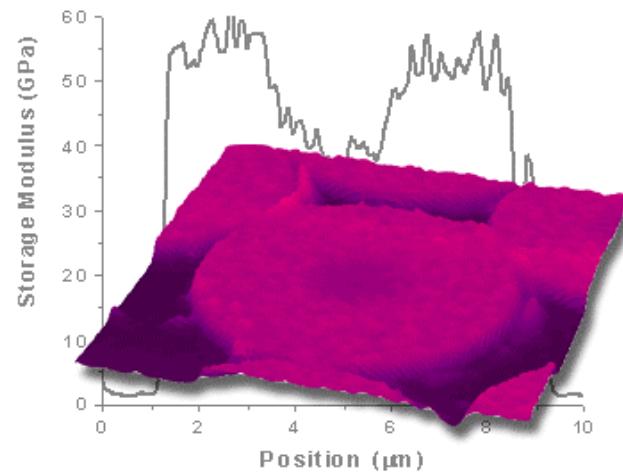
Nanomechanics



Coupling Depth-Sensing Indentation with Force Modulation & AFM Imaging



Mechanics of metal nanowires



Storage modulus image of carbon fiber/epoxy composite (10 x 10 μm)

- Locate & study **mechanics of nanoscale features**
- *Direct quantitative imaging of mechanical response* (i.e., contact stiffness & storage/loss modulus)

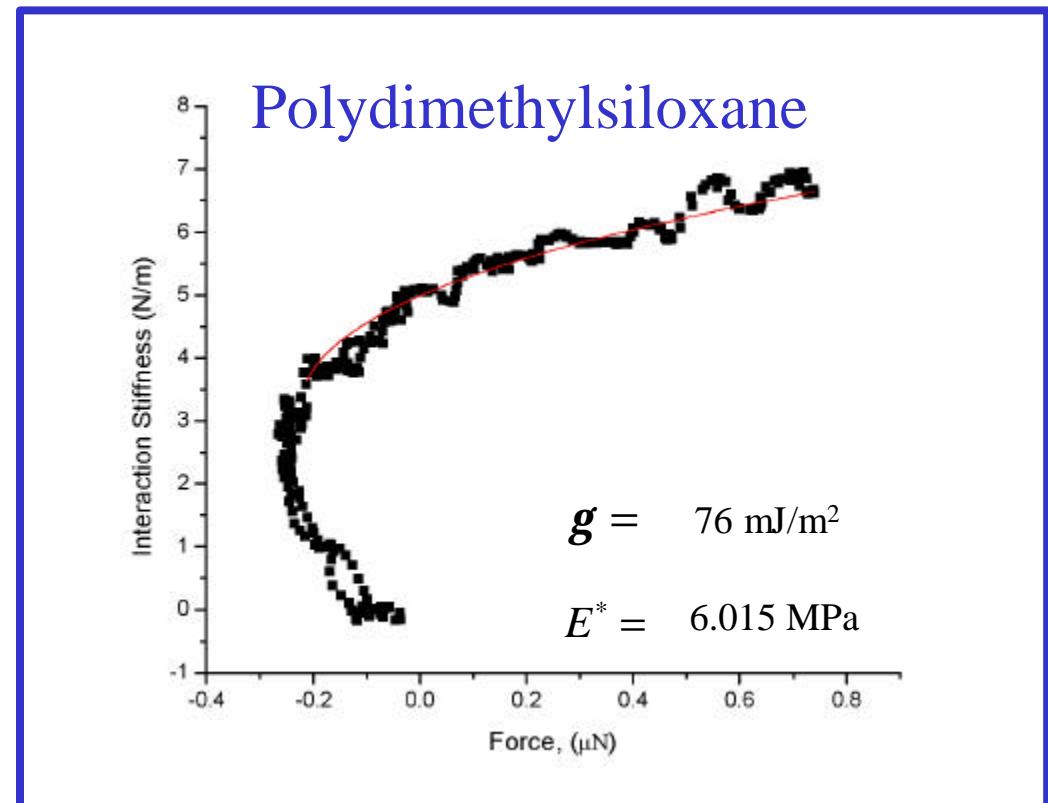
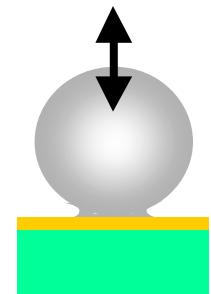
S.A. Syed Asif, K.J. Wahl, R.J. Colton & O. Warren,
J. Appl. Phys. **90**, 1192 (2001).



Nanoscale Adhesion Studies

Nano-JKR (Johnson-Kendall-Roberts) Test

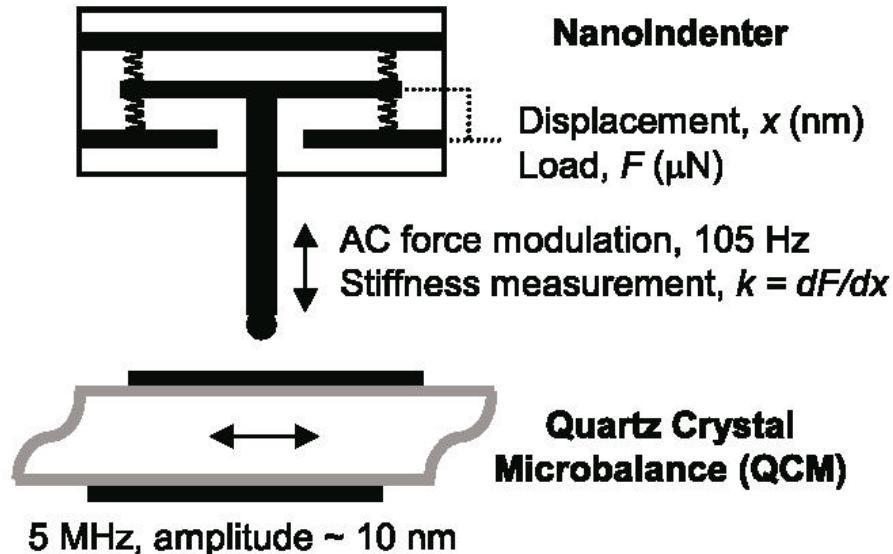
- Study formation & breaking of adhesive contacts *at scales below the optical limit*
- Measure elastic moduli (storage and loss), surface energy & strain energy release rate
- Test models & limits of continuum contact mechanics



K.J. Wahl, NRL 6176
AVS 2001



Shearing Interface Mechanics/Dynamics*



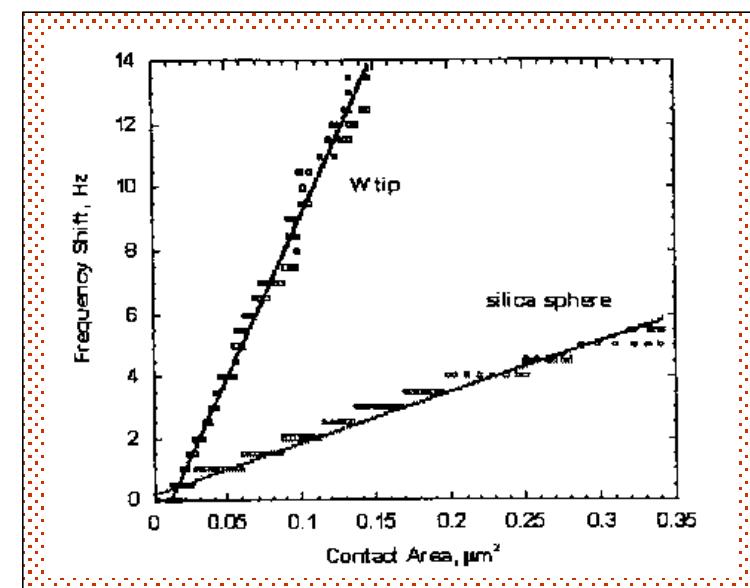
Results:

- Frequency shift of the QCM measured and modeled
 - linearly proportional to contact area
 - reflects elasticity of the interface
 - consistent with multi-contact (rough) interface

Magnitude of QCM Frequency Shift:
important parameters

- size of contact region
- degree of slippage at interface
- materials properties, rheology

Is frequency shift proportional to contact *area* or *radius*?



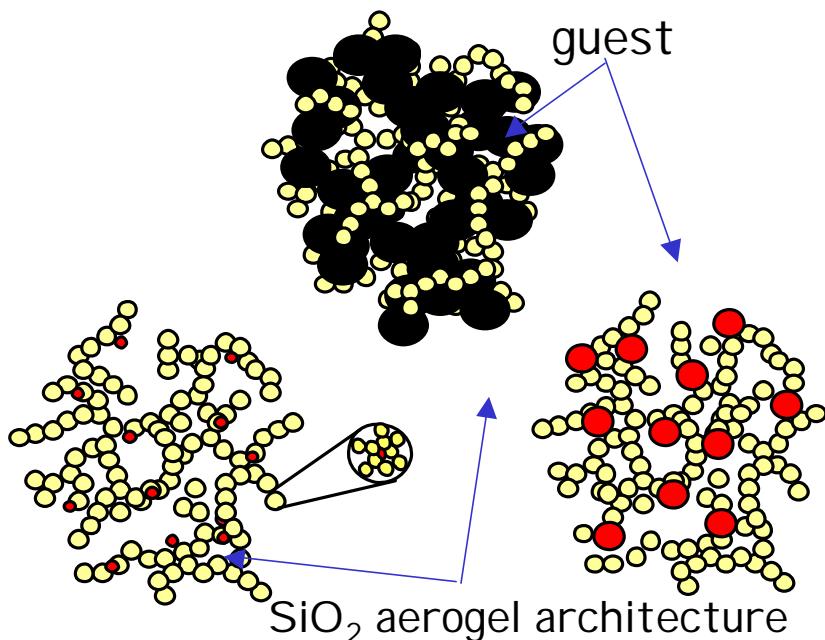
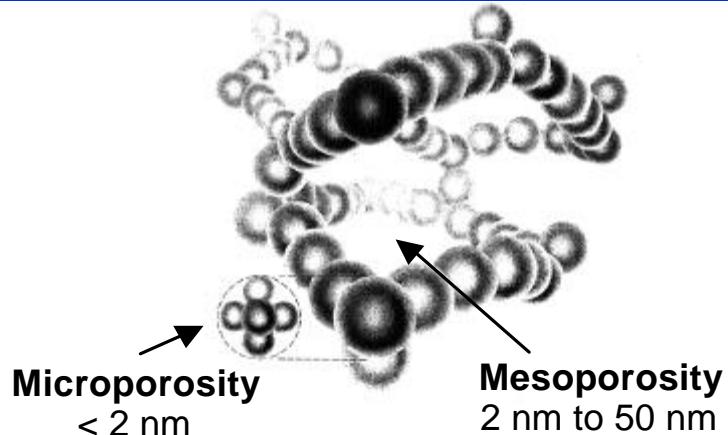
*Collaboration with NCSU; B. Borovsky, J. Krim, S.A. Syed Asif, & K.J. Wahl, *J. Appl. Phys.* **90**, 6391 (2001)



Nanostructured Mesoporous Materials

Aerogels =
Composites of Being
and Nothingness*

* J.-P. Sartre, “*L’Être et le Néant*”,
Gallimard: Paris, 1943



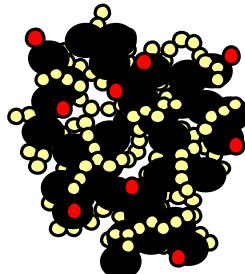
Colloidal silica as a nanoglue
where **guest particles** are
incorporated into the 3-D
structure as the silica
colloids link to form the
solid network

Morris, Anderson, Stroud, Merzbacher, Rolison,
Science **284**, 622 (1999); *Adv. Eng. Mater.* **2**, 481
(2000)



Nanostructured Mesoporous Materials

Energy Conversion

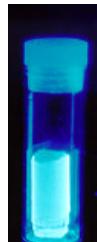


Pt/C–SiO₂ composite aerogel fuel-cell anode

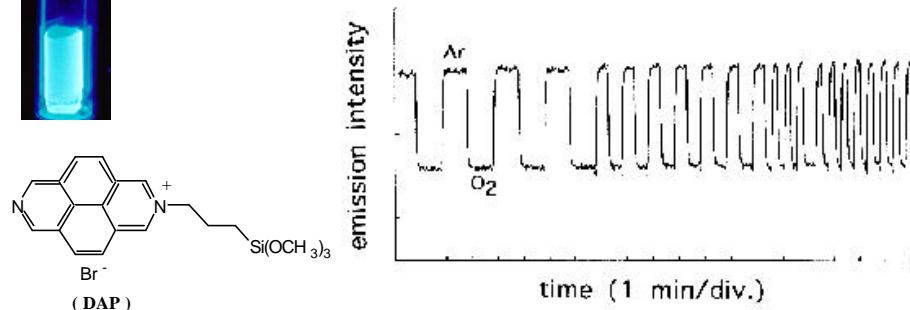
~10,000-fold improvement in catalytic activity per gram of Pt for oxidation of fuel

Anderson, Stroud, Rolison, *Nano Lett.*, in review

Superhighway for Molecules

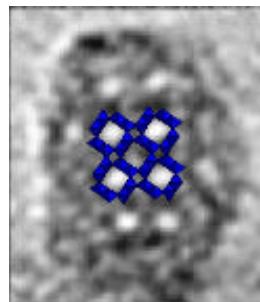


Fluorescence from diazapyrenium-modified silica aerogel

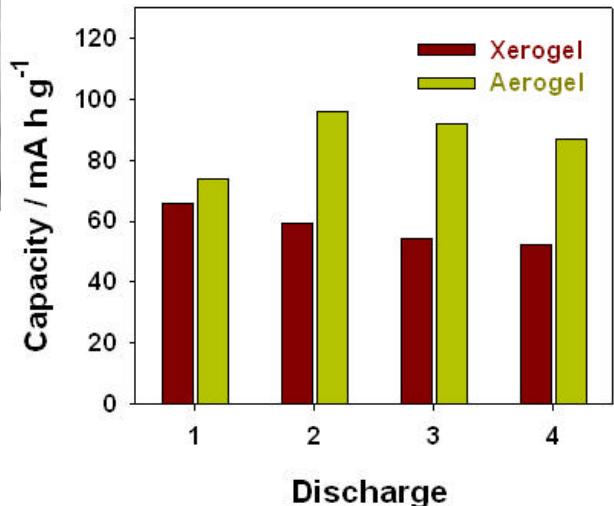


Leventis, Elder, Anderson, Merzbacher, Rolison, *Chem. Mater.* 11 (1999) 2837

Energy Storage



Cryptomelane (MnO₂) gels



Improvements in capacity for Li-ion storage and increased cell voltage for aerogel cryptomelane

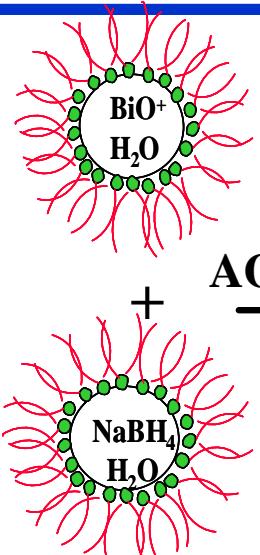
Long, Stroud, Swider-Lyons, Rolison, *Electrochem. Solid-State Lett.*, 3, 453 (2000); *J. Non-Cryst. Solids*, 285, 288 (2001)



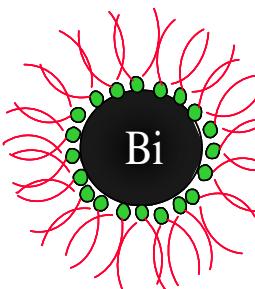
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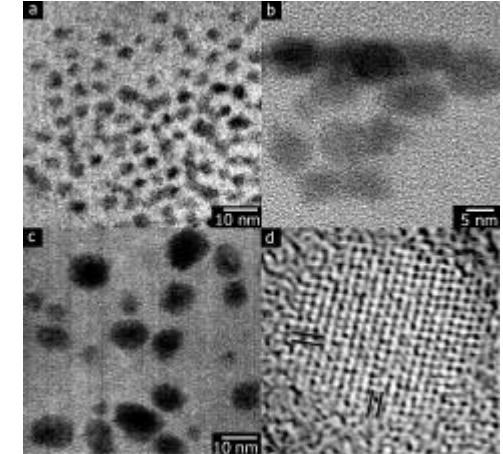
Reverse Micelles Synthesis - Nanocrystals



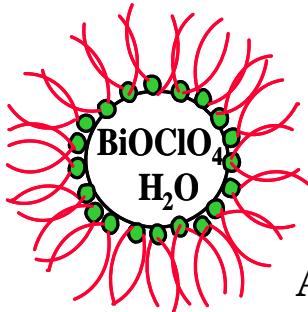
Nanocrystalline Bismuth



E. Foos, R. Stroud, A. Berry, A. Snow, P. Armistead,
J. Am. Chem. Soc. **122**, 7114 (2000).



a) 3.2 ± 0.35 nm; b) 6.9 ± 2.2 nm; c) 8.0 ± 2.7 nm

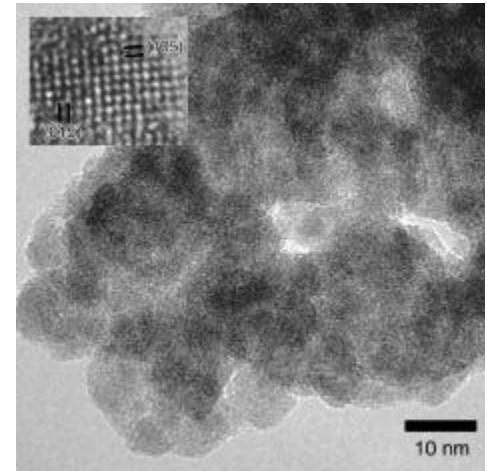


Nanocrystalline Bismuth Telluride



$\text{Te}(\text{SiMe}_3)_2$

E. Foos, R. Stroud & A. Berry,
Nano Letters, in press (27 Oct 01).



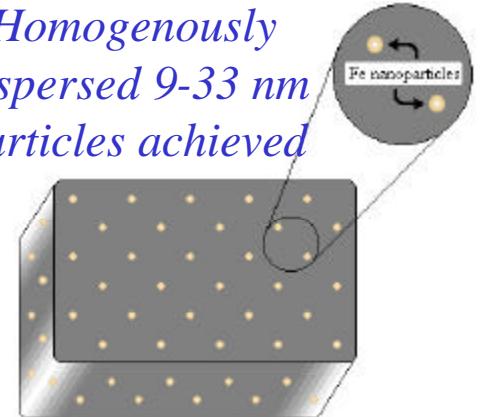
Average particle size = 4.5 nm



Metal Nanoparticle Composites

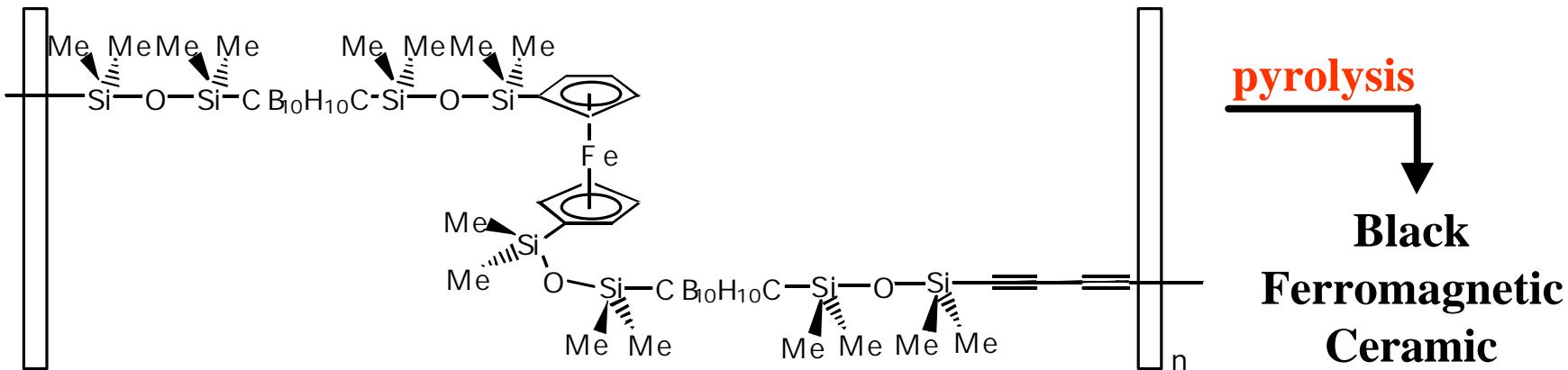
- **Objective:** Fabrication of polymer, carbon & ceramic composites with embedded metal nanoparticles
- **Approach:** Pyrolysis of organometallic containing thermosets to metal nanoparticle containing carbon & ceramic composites
- **Goal:** Composites with tailored electromagnetic properties

Homogenously dispersed 9-33 nm particles achieved



Teddy Keller, NRL Code 6127

Pyrolysis of tetramethyldisiloxyl-carborane-ferrocenylene-diacetylene polymer to form magnetic ceramic



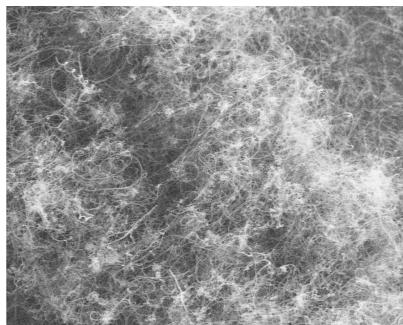


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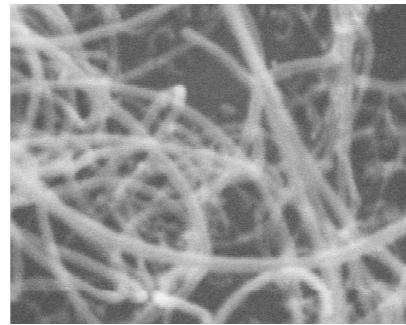


Nanofilaments: Growth, Manipulation & Assembly*

Carbon nanotubes from CVD on Fe nanoparticles (Pehrsson & Berry - 6174)

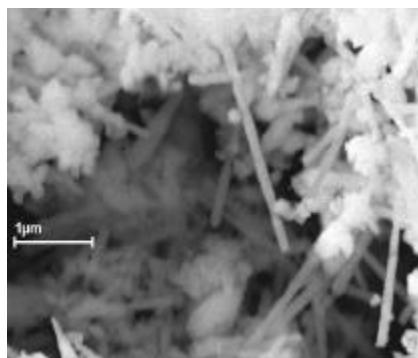


5k X



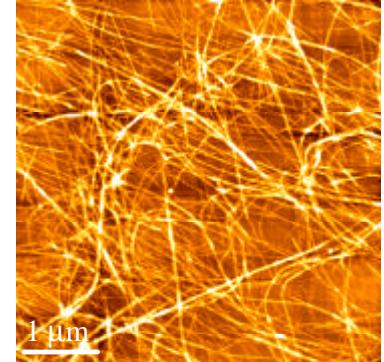
151k X

GaN nanofilaments (Purdy - 6125)

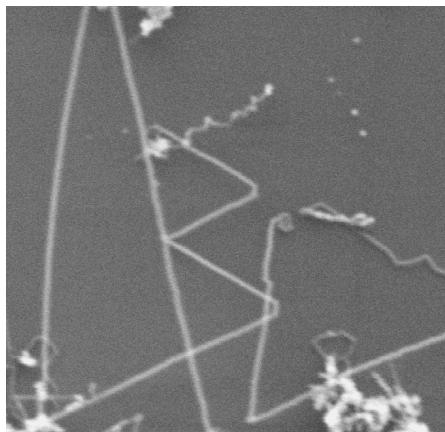


1 μm

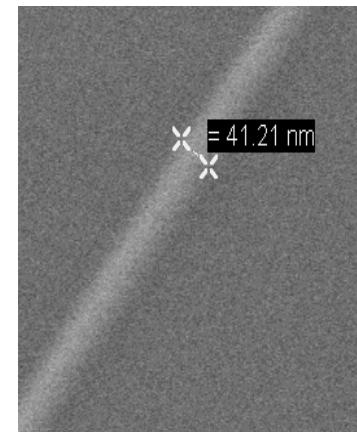
V₂O₅ nanowires (Kooi - 6177)



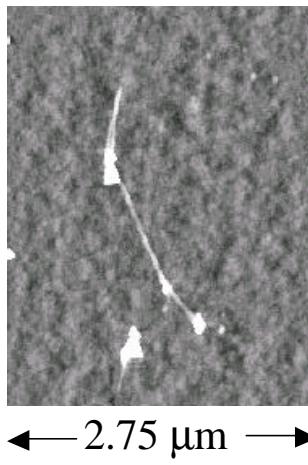
1 μm



Si nanowires grown by CVD on Au nanoparticles (Hsu-6174 & Snow-6123)



× = 41.21 nm



← 2.75 μm →

Pd (Se) nanoparticles on cNT (Long - 6125, Kooi - 6177 &

Pehrsson - 6174)

- Adsorb selectively on defects or tube ends
- Can be electroless plated or functionalized

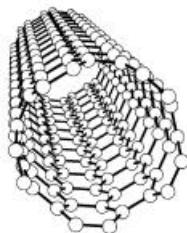
*Directed deposition/directionally controlled growth



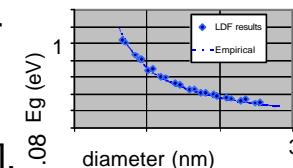
Revolutionary Carbon Nanotubes

NRL Prediction

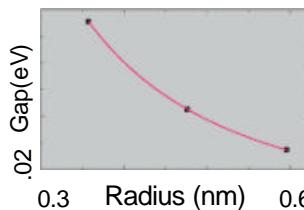
- Armchair SWNTs metallic. [Mintmire, Dunlap, White, PRL **68**, 631 (1992)]. Paper stimulated research world wide [~ 680 cites: 21 Nature, 19 Science, 46 PRL, 31CPL, 28 APL].



- Bandgaps of semiconducting SWNTs should obey an analytic relationship inversely proportional to SWNT diameter [White, Robertson, Mintmire, PRB **47**, 5485 (1993)].



- Bandgaps of quasi-metallic SWNTs are inversely proportional to the square of the SWNT diameter. [White, Robertson, Mintmire, *Clusters and Nanostructured Materials*, (Nova, NY 1996) p. 231].



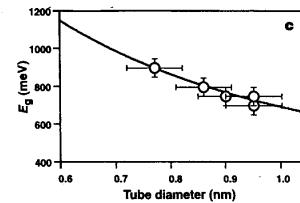
- Elastic modulus should be similar to high stiffness in-plane modulus of graphite [Robertson, Brenner, Mintmire, PRB **45**, 12592 (1992)].

Experimental Confirmation

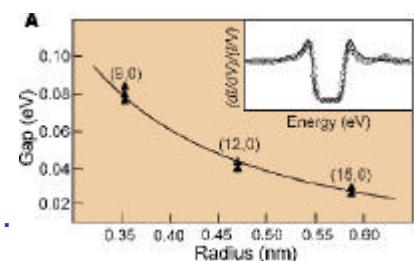
- Individual single-wall carbon nanotubes as quantum wires, [Tans, Devoret, Dal, Thess, Smalley, Geerligs, and Dekker, Nature **386**, 474 (1997)].



- Atomic structure and electronic properties of single-walled carbon nanotubes, Odom, Huang, Kim, and Lieber, Nature **391**, 62 (1998)]



- Energy gaps in “metallic” single-walled carbon nanotubes, Ouyang, Huang, Cheung, Lieber, Science **292**, 702 (2001).



- Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes, [Wong, Sheehan, and Lieber, Science **277**, 1971 (1997)].



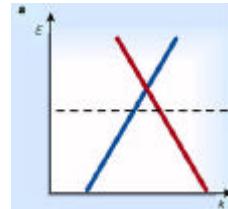
Revolutionary Carbon Nanotubes

NRL Prediction

- Stability of metallic SWNT conduction channels in presence of disorder, leading to exceptional ballistic transport properties [White, Todorov, Nature **393**, 240 (1998)].

$$\ell = \frac{6V_0^2}{(2\mathbf{s}_e^2 + 9\mathbf{s}_v^2)} N_B$$

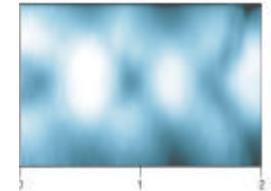
- All metallic SWNTs have a linear dispersion relation $\mathcal{E}(k)$ near the Fermi level with a slope in k vs. \mathcal{E} of $-1.88 \text{ nm}^{-1} \text{ eV}^{-1}$ [Mintmire, Dunlap, White, PRL **68**, 631 (1992); Mintmire, Robertson, White, JPCS **54**, 1835 (1993)].



- Near the Fermi level all semiconducting (metallic) SWNTs with similar diameters will have similar densities of states with the positions of the first few peaks obeying a simple analytic relation. [White, Mintmire, Nature **394**, 29 (1998); Mintmire, White PRL **81**, 2506 (1998)].

Experimental Confirmation

- Recent Confirmation: Fabry-Perot interference in a nanotube electron waveguide, [Liang et al., Nature **411**, 665 (2001)].



- Two-dimensional imaging of electronic wavefunctions in carbon nanotubes, [Lemay, et al., Nature **412**, 617 (2001)]

Expt. Slope: $-1.87 \text{ nm}^{-1} \cdot \text{eV}^{-1}$



- Spatially resolved scanning tunneling spectroscopy of single-walled carbon nanotubes, [Venema et al., PRB **62**, 5238 (2000)]



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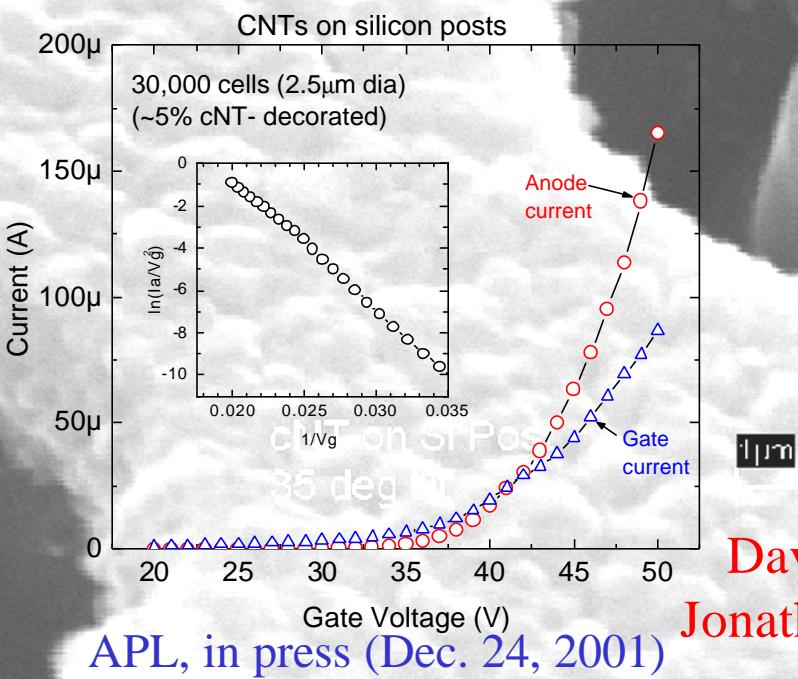
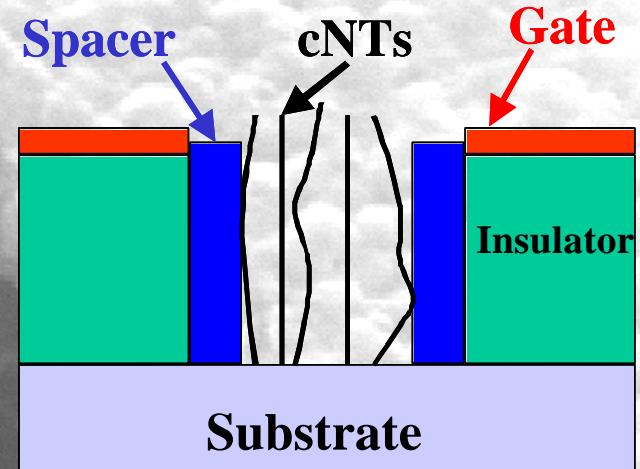
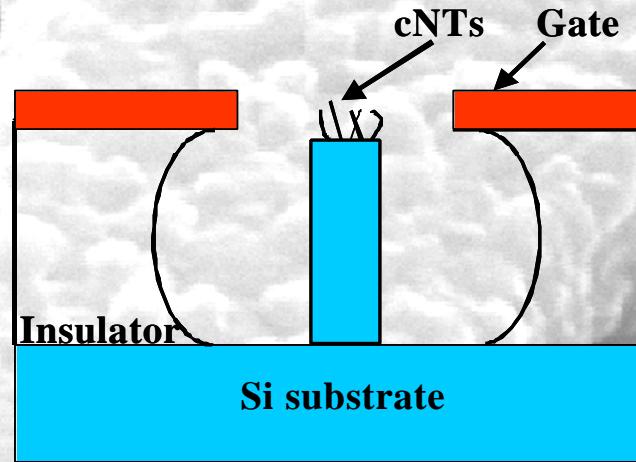
Sensors & Devices



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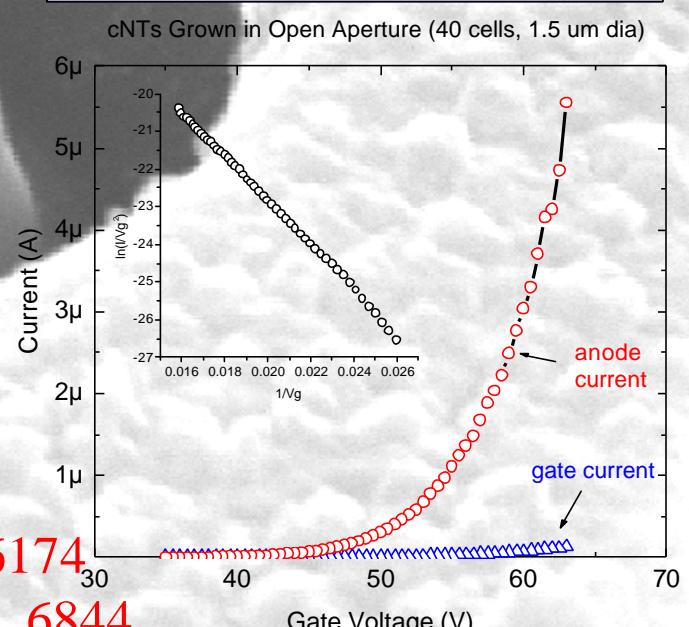


Carbon Nanotube Field Emitter Arrays



David Hsu, NRL 6174
Jonathan Shaw, NRL 6844

APL, in press (Dec. 24, 2001)



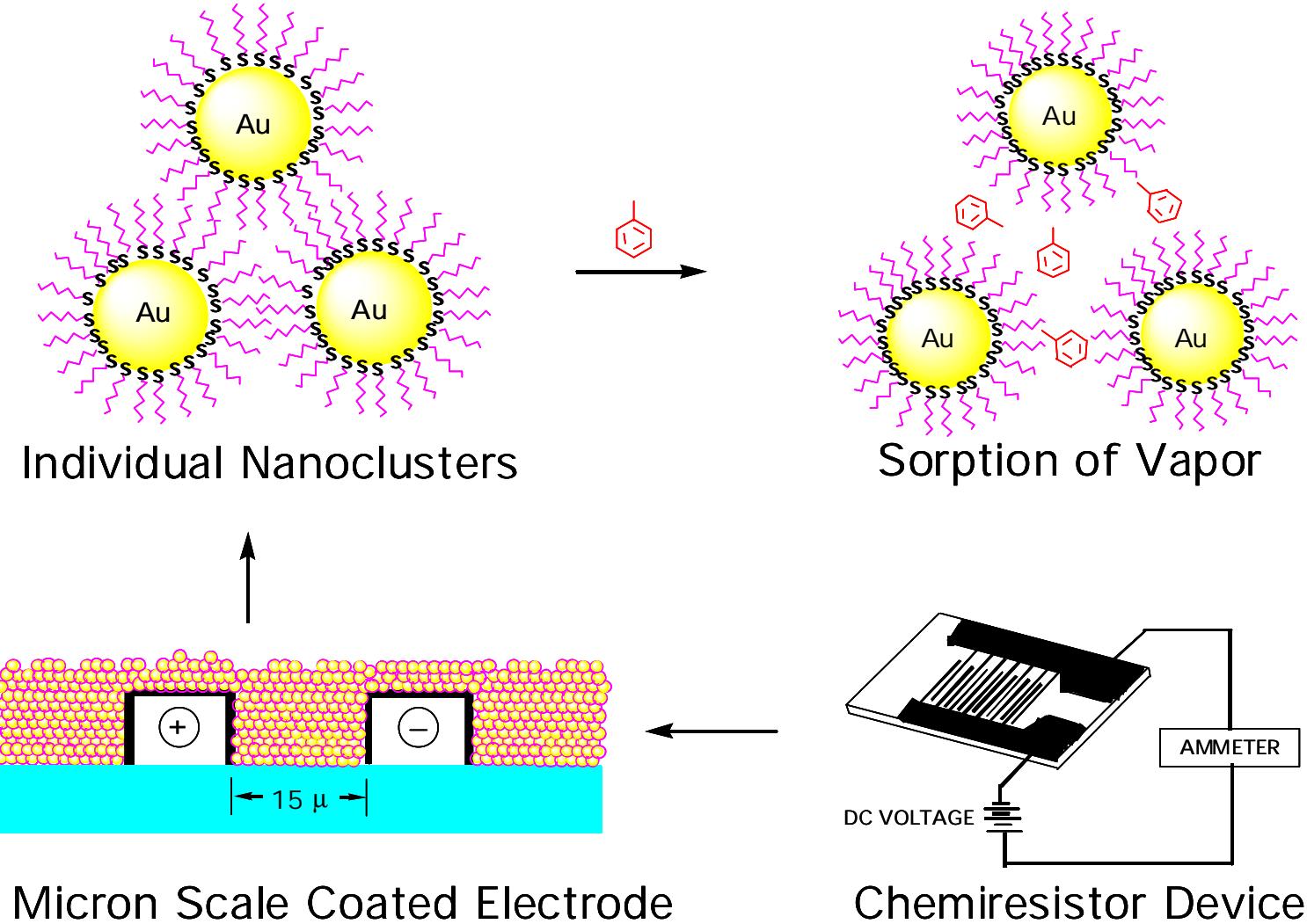


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Gold Nanocluster Chemical Sensor

A.W. Snow (NRL 6123); H. Wohltjen & N.L. Jarvis (MicroSensor Systems)



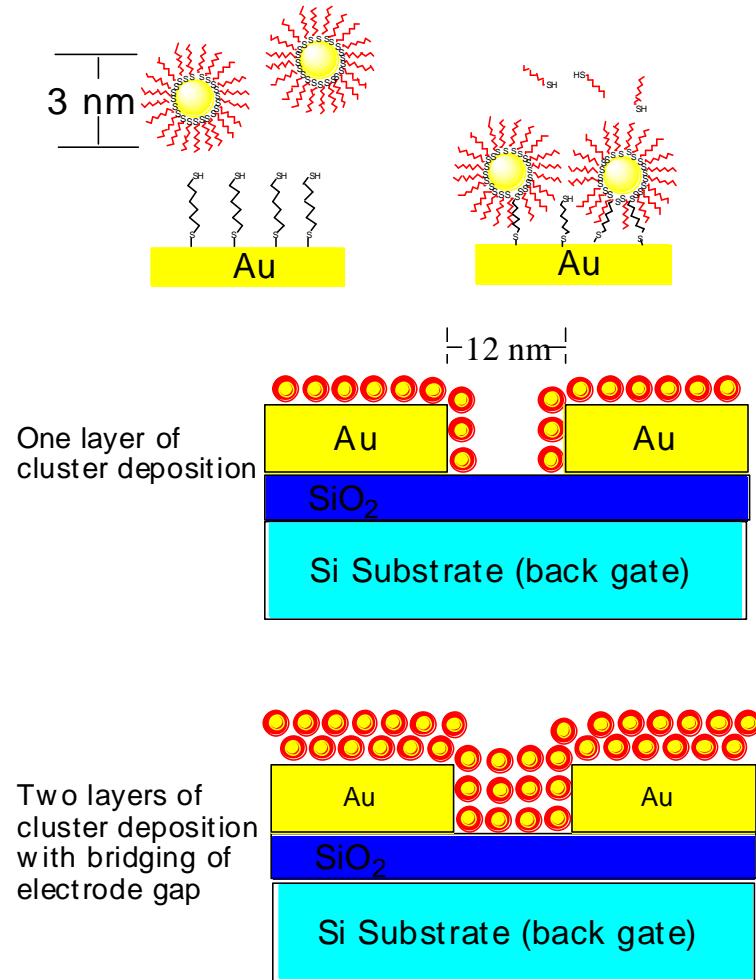


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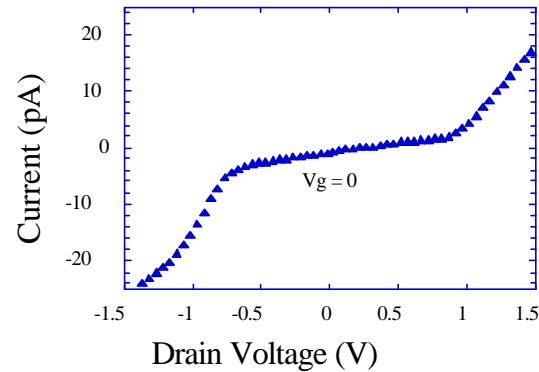


Gold Nanocluster Nanoelectronics Device

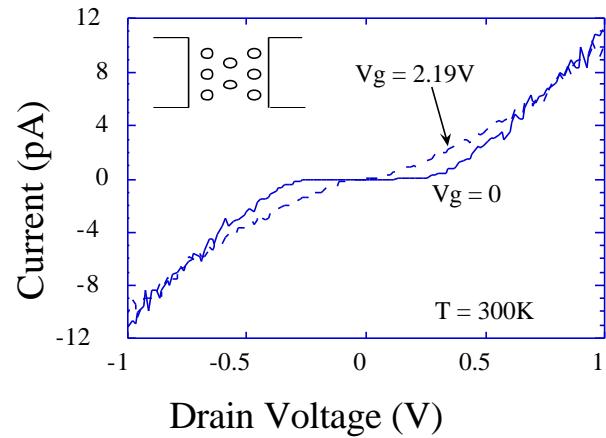
Au Nanocluster Self Assembly



Expt'l I-V Curve: Coulomb Blockade



Model I-V Curve: Switching between Gated/Non-Gated States



M.G. Ancona (NRL 6813) & W. Kruppa (NRL 6851); A. Snow & E. Foos (NRL 6123)



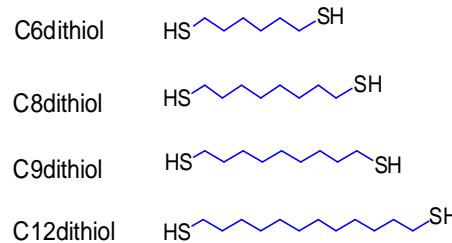
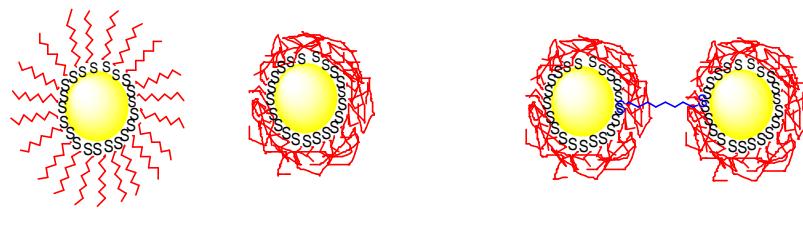
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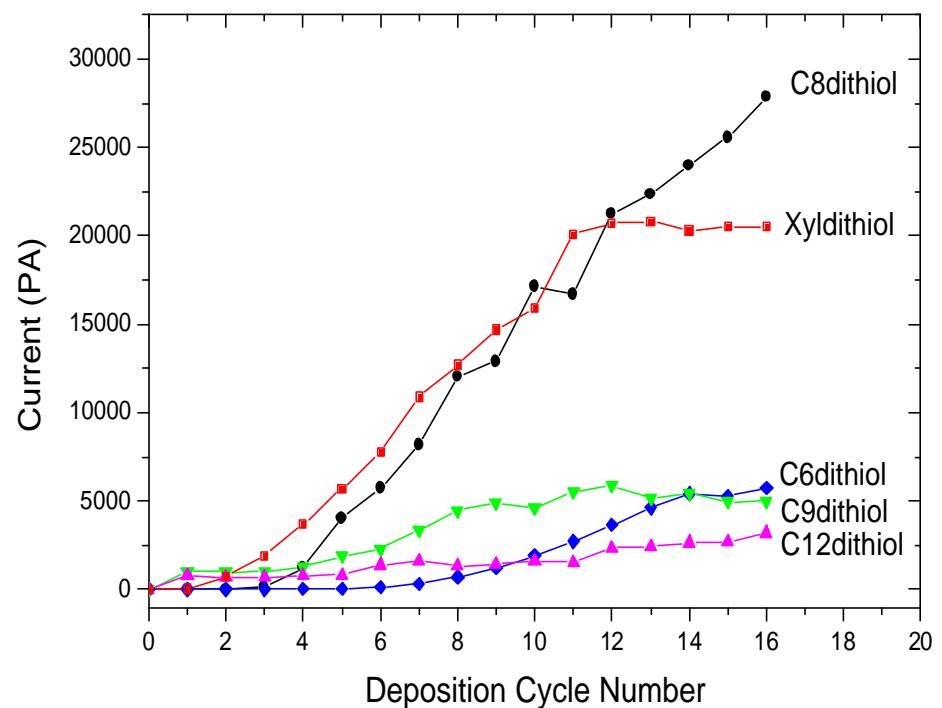
Au Nanocluster – Intercluster Conductivity

A.W. Snow, M.G. Ancona, W. Kruppa, E. Foos

Cluster Ligand Shell and Alkanedithiol Coupling Agent Dimensions
Critical to Layered Self-Assembly and Conductance Issues



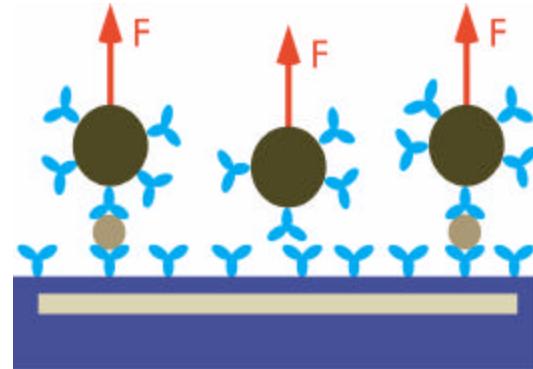
Dithiol Chain Length Variation Effect on Cluster Self-Assembly onto Substrate Electrode and Conductance



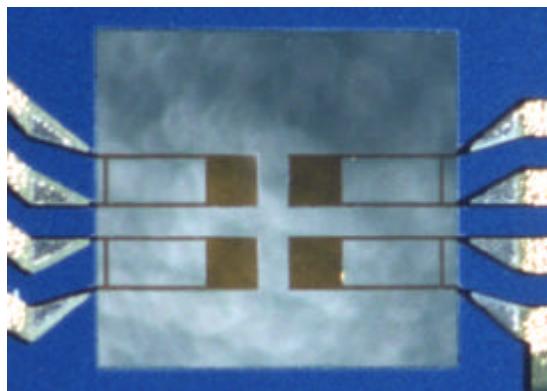


Single Molecule Biosensors

Force Discrimination Assay

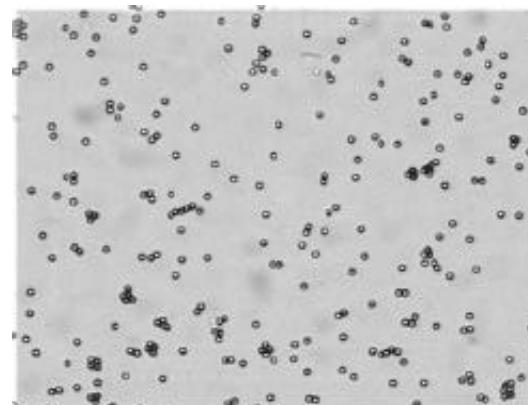


Biosensor Platforms



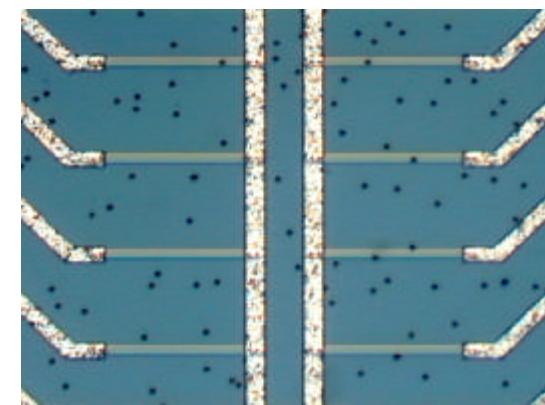
Piezoresistive
cantilever
FABS

D.R. Baselt, *et al.*, *Proc. IEEE* **85**, 672 (1997)



Transparent substrate
with optical detection
FDB

G.U. Lee, *et al.*, *Anal. Biochem.* **287**, 261 (2000)

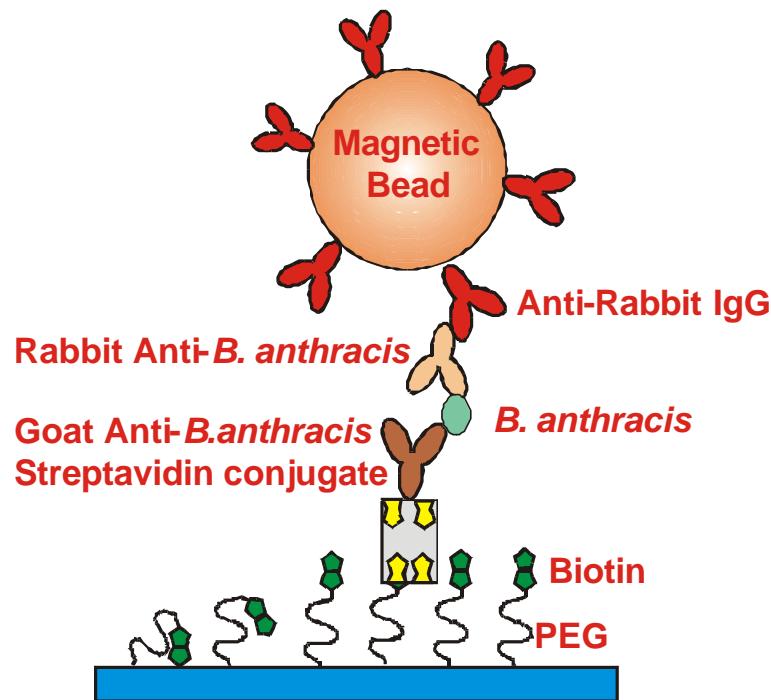
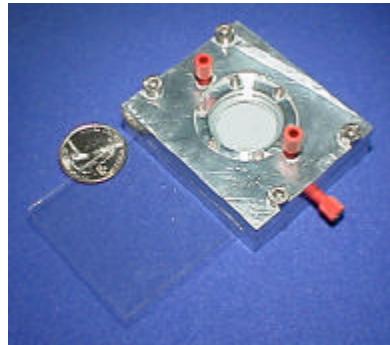


Magnetoresistive
elements
BARC

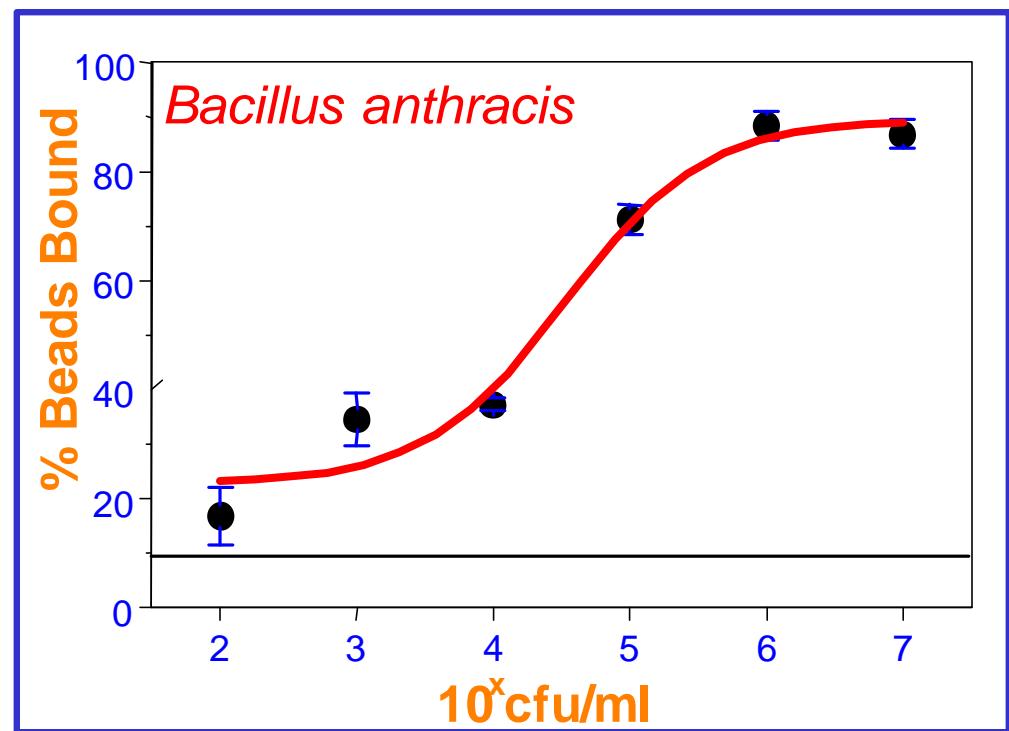
R.L. Edelstein, *et al.*, *Biosensors & Bioelectronics* **14**, 805 (2000)



Single Molecule Biosensors - FDB

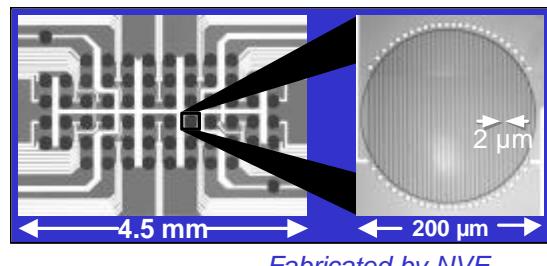


C. Cole, R. Colton, M. Malito, S. Mulvaney,
M. Natesan, C. Tamanaha & L. Whitman –
NRL 6177

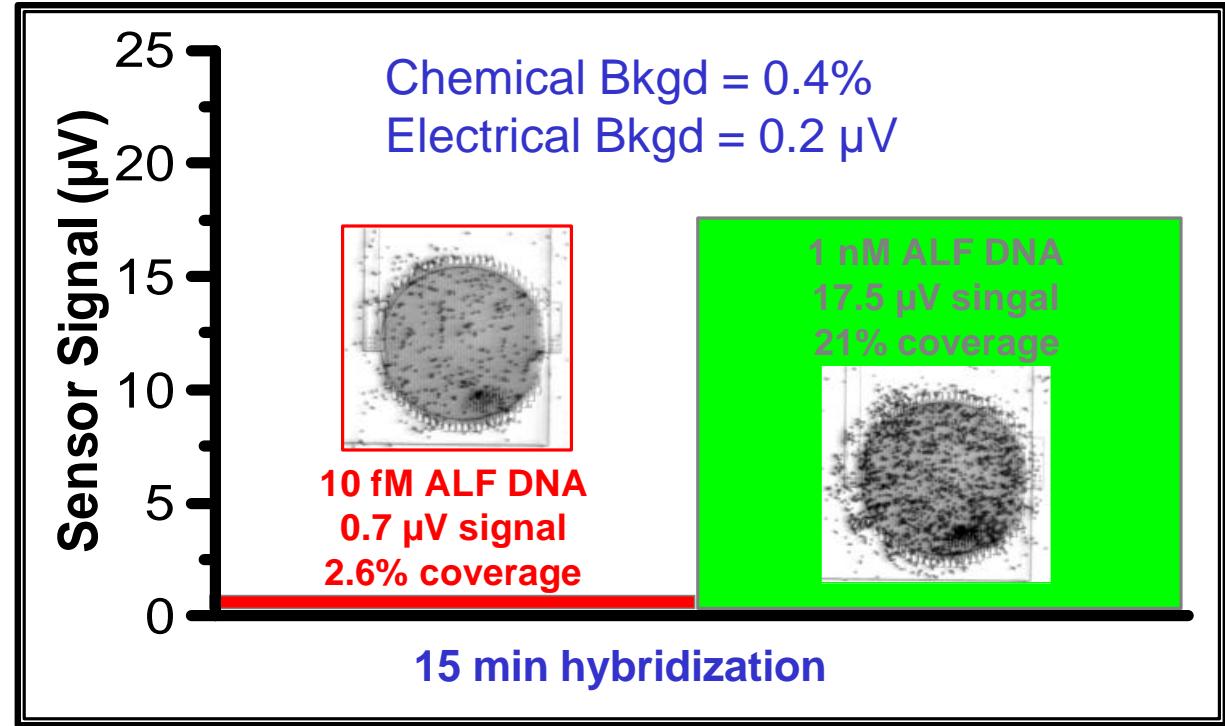
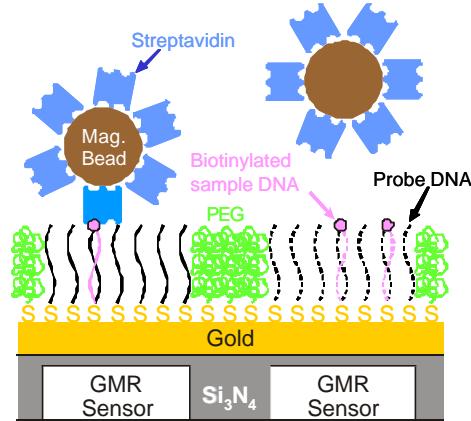




Single Molecule Biosensors - BARC



Fabricated by NVE



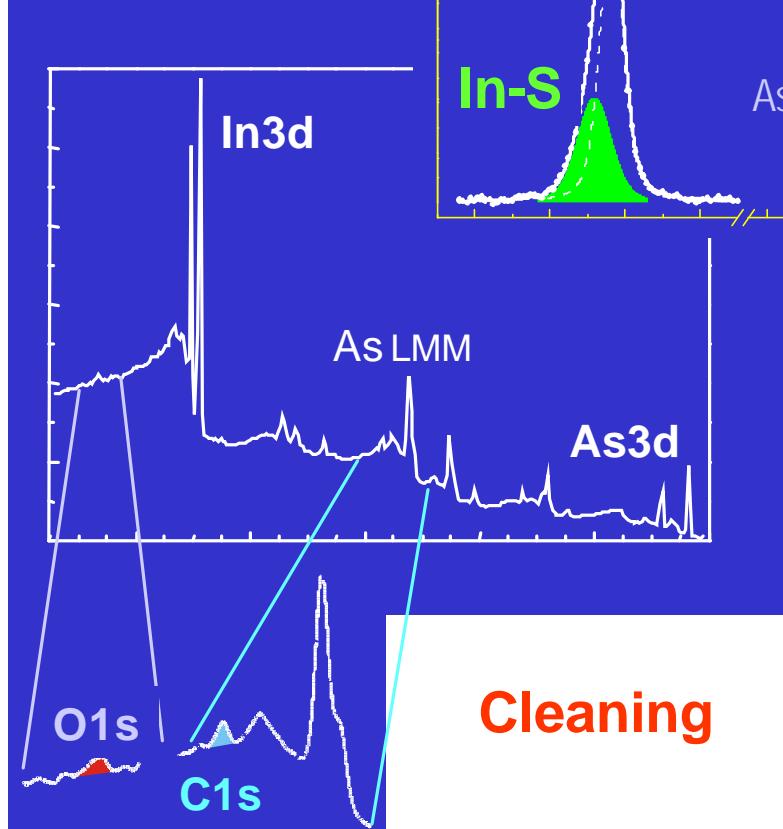
- Demonstrated sensitivity <10 fM in ~30 min total assay time
- Preliminary sensitivity with PNA-DNA hybridization:
0.1 fM, in 30 μl sample volume = 3 zmol = 1800 molecules



InAs Nanowire for Electronics/Biosensors

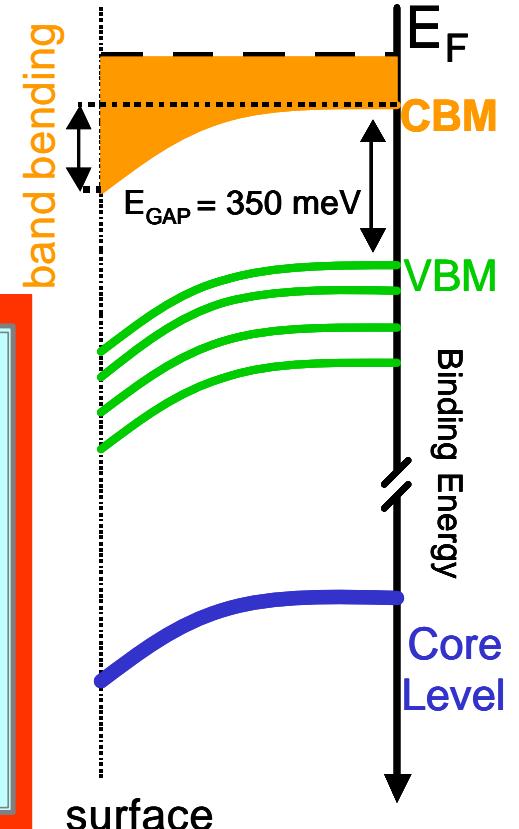
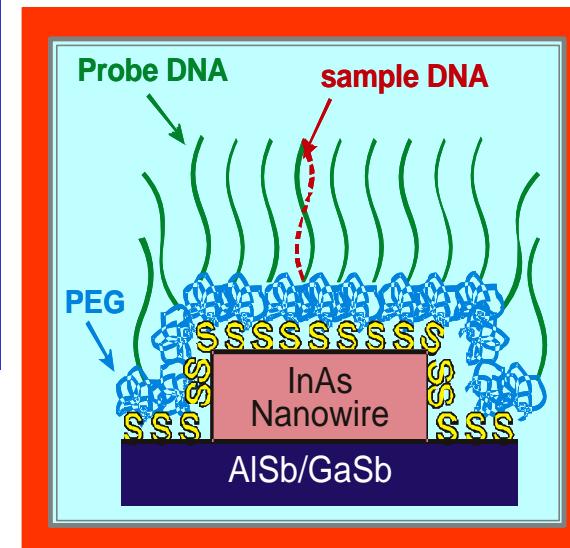
“Beaker Chemistry”

Passivation



Electronic Properties

Charge Accumulation Layer



D.Y. Petrovykh (UMD/NRL 6177), M.J. Yang (NRL 6876); L.J. Whitman (NRL 6177)